THE VALENCE ISOMERIZATION OF 9,10-DIPHENYL-1,2,3,4-TETRAHYDRO-2,1,4-ETHANYLYLIDENENAPHTHALENE

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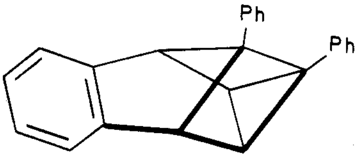
Summary

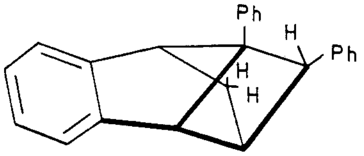
9,10-Diphenyl-1,2,3,4-tetrahydro-2,1,4-ethanylylidenenaphthalene (II) isomerizes at 160–250° to give 1-(*cis*-1,2-diphenylethenyl)-1,2-dihydronaphthalene (IV). The structure of (IV) is supported by its p.m.r., u.v., and mass spectra, as well as by its conversion into 1-(1,2-diphenylethyl)naphthalene (V) and into 1-(*cis*-1,2-diphenylethenyl)naphthalene (VII) by palladium and palladium–nitrobenzene, respectively. Compounds (V) and (VII) have been synthesized independently from 1-(1-naphthyl)-1,2-diphenylethanol (VI).

INTRODUCTION

In a preliminary communication it was reported that 1,8-diphenyl-1a,2,7,7a-tetrahydro-1,2,7-metheno-1*H*-cyclopropa[*b*]naphthalene (I), the "naphthalene–tolan photo-adduct", reacted with hydrogen at atmospheric pressure in the presence of palladium on carbon to give in almost quantitative yield a dihydro derivative, which was suggested to be 9,10-diphenyl-1,2,3,4-tetrahydro-2,1,4-ethanylylidenenaphthalene (II).[1] It has now been found that this hydrocarbon isomerizes when heated. The rearrangement occurs at a detectable rate at *c.* 160° and is conveniently carried out on a preparative scale at 200–250°, when it is complete in less than 10 min. Under these conditions the formation of only one product could be detected.



(I)



(II)

DISCUSSION

The isomerization of (II) is accompanied by characteristic changes in its spectroscopic properties. Thus, the u.v. spectrum of the hydrocarbon (II) exhibits features which are characteristic for an indane derivative,[2] λ_{max} at 260 mμ (ϵ 1300),

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[1] Sasse, W. H. F., Collin, P. J., and Sugowdz, Galina, *Tetrahedron Lett.*, 1965, 3373.

[2] Scott, A. I., "Interpretation of the Ultra-violet Spectra of Natural Products." Ch. 3. (Pergamon Press: Oxford 1964.)

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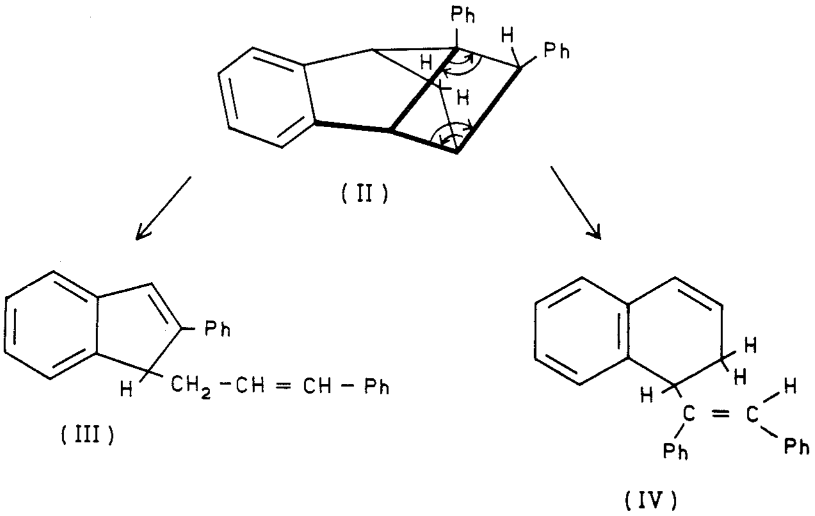
268 mμ (ε 1500), and 275 mμ (ε 1470), while the spectrum of the rearranged compound has a broad maximum which occurs near 260 mμ (ε 18300). The latter spectrum was ascribed to the dihydro compound (II)[1] until it was known that (II) rearranges quantitatively under the conditions which were used for its purification (preparative gas chromatography at 275°).

The p.m.r. spectrum of the rearranged dihydro compound indicates the presence of 14 aromatic protons (complex multiplet between 6·6 and 7·3 p.p.m.), three non-equivalent olefinic protons [centred at 6·36 p.p.m. (doublet of triplets, separated by 9·6 and 1·5 c/s), at 6·11 p.p.m. (doublet; separation *c.* 0·8 c/s), and at 5·76 p.p.m. (doublet of triplets, separation 9·6 and 4·3 c/s)], one proton [centred at 3·89 p.p.m. (broadened triplet, separation 7·2 c/s)], and two methylene protons (approximately a doublet of doublets centred at 2·36 p.p.m.; separation 7·3, 4·4, and 1·6 c/s).

First-order analysis led to closer examination of two structures, namely (III) (cf.[3]) and (IV), which can be derived formally from the dihydro derivative (II) by two alternative modes of valence isomerization:



Although the u.v. spectrum of the rearranged hydrocarbon was consistent with the dihydronaphthalene structure[4a] (IV), spectral data for suitably related model compounds were lacking* and this made it desirable to obtain chemical

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* The chemical-shift positions and splitting patterns of the non-aromatic protons in the p.m.r. spectrum of (IV) agree well with the spectrum of 1,2-dihydronaphthalene,[5] which was made available to the authors, after completion of the present work, through the courtesy of Professor A. R. Katritzky.

[3] Dressler, H., and Kurland, R. J., *J. org. Chem.*, 1964, **29**, 175.

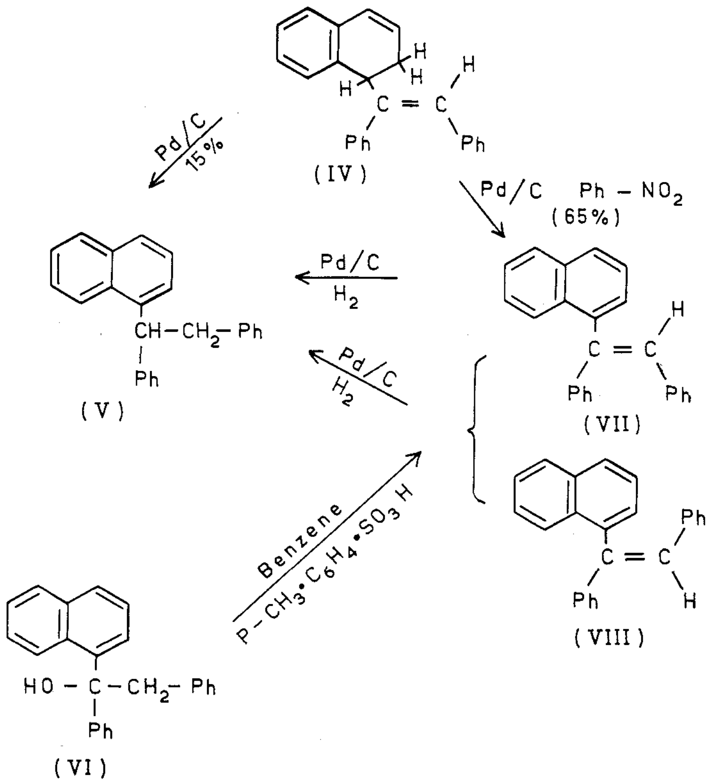
[4] Friedel, R. A., and Orchin, M., "Ultra-violet Spectra of Aromatic Compounds." (*a*) Spectrum No. 29. (*b*) Spectra Nos. 125 and 126. (John Wiley: New York 1957.)

[5] Katritzky, A. R., and Semple, B., personal communication.

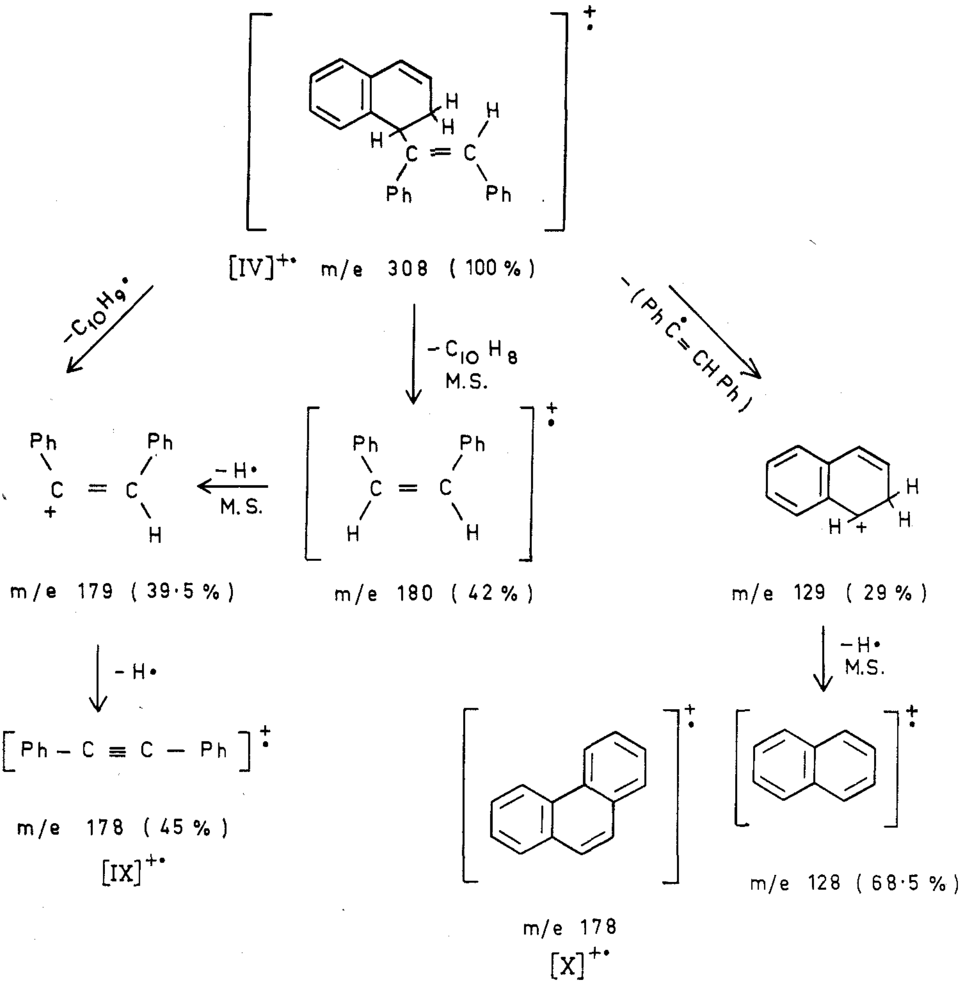
evidence on which to base the structural assignment. Two attempts to dehydrogenate the rearranged hydrocarbon are now described.

At 275° and in the absence of solvent, the action of palladium on carbon produced *inter alia* an isomeric hydrocarbon, the u.v. and p.m.r. spectra of which suggested that it was 1-(1,2-diphenylethyl)naphthalene (V). This assignment was confirmed by an unambiguous synthesis of (V), which involved the dehydration of the known carbinol (VI) in boiling benzene with *p*-toluenesulphonic acid followed by hydrogenation of the resulting mixture of the olefins (VII) and (VIII).

Dehydrogenation with palladium on carbon in nitrobenzene at 190° gave one of the two stilbenes [(VII) or (VIII)] already encountered in the dehydration of the carbinol (VI) in 60–65% yield. This compound had the retention time of the minor isomer formed in the dehydration of (VI), and on catalytic hydrogenation it gave the ethane (V) in quantitative yield. These results, which are summarized in Scheme 1, provide unequivocal evidence in support of the structure (IV) for the valence isomer of the dihydro derivative of the naphthalene-tolan photo-adduct (I). This assignment accords also with the mass spectrum of the rearranged hydrocarbon, the most abundant ions of which can be accounted for by postulating the following three different modes of fragmentation of the molecular ion (Scheme 2):



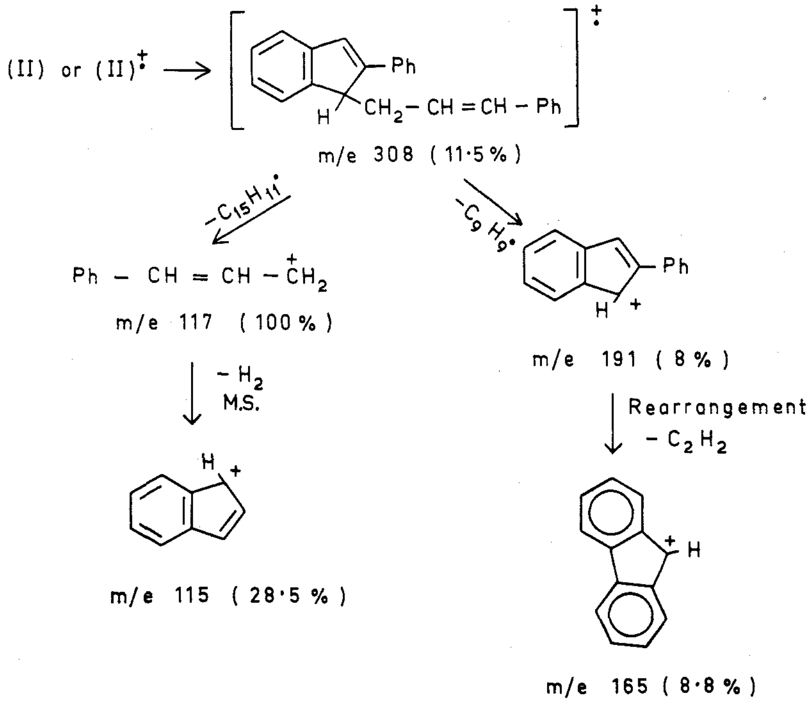
Scheme 1



Scheme 2

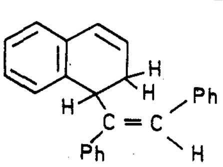
For each of the ions at *m/e* 180, *m/e* 179, and *m/e* 178 an alternative structure based on phenanthrene can be written (for example, $[X]^{+\cdot}$ instead of $[IX]^{+\cdot}$ for *m/e* 178), but this ambiguity does not affect the structural assignment proposed for (IV).

As expected, the mass spectrum of the hydrocarbon (II) reveals all the peaks observed in the mass spectrum of its valence isomer (IV). However, several ions that do not contribute to any extent to the spectrum of (IV) occur in the spectrum measured with (II). Thus, for example, the most abundant ion in the spectrum of (II) occurs at *m/e* 117 and loses H_2 to give an ion at *m/e* 115, as indicated by a metastable peak at *m/e* 113·0. Other ions of relatively high abundance, which occur in the spectrum of (II) but are lacking with (IV), occur at *m/e* 191 and *m/e* 165. These ions can readily be accounted for if it is assumed that (II) rearranges in the mass spectrometer, either thermally or upon electron impact, into the alternative valence isomer (III) as well as (IV). Subsequent reactions of the molecular ion of (III) (outlined in Scheme 3) will give rise to the additional ions in the mass spectrum of (II) mentioned above.



Scheme 3

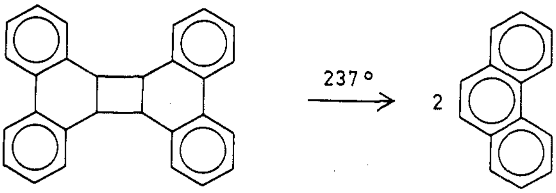
Comparison of the u.v. spectra of the stilbenes (VII) and (VIII) shows that the compound derived from (II) absorbs at longer wavelengths ($\lambda_{\max}$ at 295–297 mμ, ϵ 14400) than the isomer ($\lambda_{\max}$ at 284–286 mμ, ϵ 13100) which is formed as the main product in the dehydration of the carbinol (VI). Inspection of molecular models shows that structure (VII) with two *cis* phenyl groups is sterically less crowded than the isomer (VIII). This suggests that the product of the palladium-catalysed dehydrogenation of the valence isomer of (II) by nitrobenzene is 1-(*cis*-1,2-diphenylethenyl)naphthalene (VII). As it is not known whether the geometry of the stilbene moiety in (IV) [or in (VII)] remains unaltered during this reaction, the stereochemistry of (IV) cannot be deduced from that of (VII). Nevertheless, the opening of the cyclobutane ring in (II) should produce—at least initially—the *cis* compound (IV) rather than the *trans* isomer (XI). In fact, the u.v. spectrum of the rearranged hydrocarbon appears to favour the *cis* structure. Thus, for instance, at 300 mμ, a point where the molecular extinction coefficients of *cis*- and *trans*-stilbene differ markedly,[4b] the combined extinction coefficients of 1,2-dihydronaphthalene[4a] and *cis*-stilbene (*c*. 8000) are closer to that of the rearranged dihydro derivative of (II) (*c*. 4500) than the sum of the extinctions of 1,2-dihydronaphthalene and *trans*-stilbene



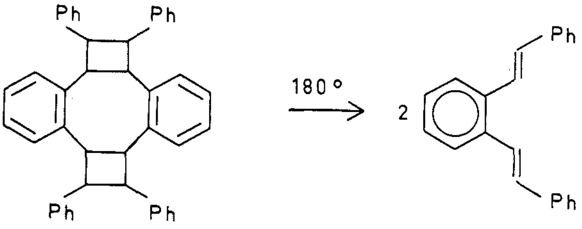
(XI)

(*c.* 22500). On this basis it is postulated that the valence isomerization of 9,10-diphenyl-1,2,3,4-tetrahydro-2,1,4-ethanylylidenenaphthalene (II) between 160° and 250° produces 1-(*cis*-1,2-diphenylethenyl)-1,2-dihydronaphthalene (IV).

Two aspects of the conversion of (II) into (IV) invite comment. Firstly, the temperature at which this isomerization can be detected (*c.* 160°) is below that required for the cleavage of the majority of cyclobutanes.[6] Thus, simple cyclobutanes are cleaved to ethylenes at temperatures of *c.* 400°. One factor which may contribute to the greater thermal stability of (IV) compared with (II) is that, of the double bonds formed in the former, one is conjugated with one phenyl group and the other with two. The importance of this effect is reflected in the relative ease with which compounds such as (XII)[7] and (XIII)[8] are cleaved into the corresponding olefins:



(XII)



(XIII)

Inspection of Dreiding molecular models shows that the relief of strain associated with ring opening in (XII) and (XIII) is not significantly greater than in simple monocyclic cyclobutane derivatives. In contrast, the tricyclic system in (II) can be formed only at the expense of considerable deviation from the bond angles characteristic of cyclobutane. This would suggest that relief of strain accompanying the isomerization of (II) may be an additional driving force for this valence isomerization. Finally, it may be noted that Büchi and Goldman[9] rearranged the ketone (XIV), which is structurally related to (II), at 475° to the cyclopentene (XV). It is not known whether this isomerization proceeds at lower temperatures. The corresponding isomerization in the present case would lead to the indene (III), as postulated above in the interpretation of the mass spectrum of (II).

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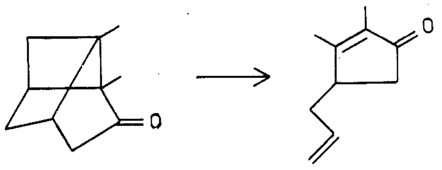
[6] Breslow, R., in "Molecular Rearrangements." (Ed. P. de Mayo.) Vol. I, p. 245. (John Wiley: New York 1963.)

[7] Wittig, G., Koenig, G., and Clauss, K., *Liebigs Ann.*, 1955, **593**, 127.

[8] Müller, E., Sauerbier, M., and Heiss, J., *Tetrahedron Lett.*, 1966, 2473.

[9] Büchi, G., and Goldman, I. M., *J. Am. chem. Soc.*, 1957, **79**, 4741.



(XIV) (XV)

EXPERIMENTAL

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Infrared spectra were determined in carbon tetrachloride with a Perkin–Elmer Infracord 337. The same solvent was used also for the determination of p.m.r. spectra at 60 Mc/s with a Varian A60 n.m.r. spectrometer. Tetramethylsilane was employed as internal standard. Ultraviolet spectra were measured in cyclohexane with a Perkin–Elmer Spectracord 4000A. Mass spectra were measured with an Atlas CH4 mass spectrometer. Separations involving gas chromatography were carried out at 275° with a 10-ft column packed with Chromosorb-W, impregnated with SE-30 (10%). X4 solvent is a petrol fraction, b.p. 56–73°, containing 1 vol. % of aromatics. X60 is a petrol fraction, b.p. 61–88°, containing 6 vol. % of aromatics. The palladium catalyst was obtained from Engelhardt Industries Ltd, Baker Platinum Division, London. The silicic acid used was obtained from Mallinckrodt (100 mesh; A. R.).

Hydrogenation of the Naphthalene–Tolan Photo-Adduct (I)

A solution of (I) (0·1 g) in cyclohexane (10 ml) was hydrogenated at atmospheric pressure in the presence of palladium on carbon (5%; 0·1 g). The equivalent of one mole of hydrogen was taken up in 5–7 min. After removal of the catalyst the solvent was distilled off at 20–40° at 0·1 torr to give a colourless viscous gum (0·095 g) of *9,10-diphenyl-1,2,3,4-tetrahydro-2,1,4-ethanylylidenenaphthalene* (II) (Found: C, 93·3; H, 6·2. $C_{24}H_{20}$ requires C, 93·6; H, 6·5%). Attempts to induce crystallization failed. The analytical sample was prepared by hydrogenation of an analytical sample of (I) in analytically pure cyclohexane as described above. Attempts to purify (II) by high-vacuum distillation, molecular distillation, or preparative gas chromatography produced the rearranged compound (IV). The p.m.r. spectrum of (II) has been described and discussed[1] elsewhere; the u.v. and mass spectra are described in the Discussion section of the present paper.

Thermal Rearrangement of 9,10-Diphenyl-1,2,3,4-tetrahydro-2,1,4-ethanylylidenenaphthalene

The dihydro derivative (0·09 g) (II) was transferred to a Pyrex test tube and freed of solvent and air. The test tube was then immersed in a bath which had been preheated at 250 ± 10°. After being kept at this temperature for 10 min the test tube was cooled and the products were dissolved in light petroleum (fraction X60). The resulting solution was passed through a short bed of silicic acid (1·5 by 3 cm). The first fraction to be eluted formed a colourless viscous gum (0·09 g) which could not be induced to crystallize. An analytical sample of *1-(*cis*-diphenylethenyl)-1,2-dihydronaphthalene* (IV) was prepared by short-path distillation (block temperature 235° at 0·08 mm) (Found: C, 93·2; H, 6·1. $C_{24}H_{20}$ requires C, 93·6; H, 6·5%). The u.v., mass, and p.m.r. spectra of this compound are mentioned in the Discussion section.

*Action of Palladium on Carbon on 1-(*cis*-1,2-Diphenylethenyl)-1,2-dihydronaphthalene*

(i) *In the absence of solvent.*—Freshly rearranged (IV) (from 0·1 g of (II)) was degassed and heated with palladium on carbon (5%; 0·05 g) at 275° for 45 min. The reaction mixture was extracted with boiling benzene, freed of solvent, and chromatographed in light petroleum (fraction X4) on alumina (100 g). The first fractions (0·015 g) were liquid and contained, besides the naphthalene (VI), at least one other hydrocarbon with benzylic protons (p.m.r.).

Subsequent fractions were homogeneous as indicated by thin-layer chromatography; crystallization from methanol gave colourless prisms of 1-(1,2-diphenylethyl)naphthalene (V)

(0·015 g), m.p. 81–81·5°. The spectroscopic properties of this sample were identical with those of an authentic specimen, m.p. 83·5–84°, and the m.p. of a mixture of the two was 81–81·5°.

(ii) *In the presence of nitrobenzene.*—The naphthalene–tolan adduct (I) (1·0 g) was hydrogenated and rearranged as described. The degassed product (II) was heated with freshly purified nitrobenzene and palladium on carbon (5%; 0·5 g) in an atmosphere of nitrogen at 200–210° (bath) for 40 min. The residue left after removal of the nitrobenzene by steam distillation was extracted with benzene, filtered, and freed of solvent. Chromatography on silicic acid (15 g) in light petroleum (fraction X4) gave as first fraction after crystallization from ethanol *1*-(cis-*1,2-diphenylethenyl)naphthalene* (*VII*) (0·55 g) as colourless prisms, m.p. 86–87° (Found: C, 93·8; H, 5·6. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%). The u.v. spectrum exhibited a broad maximum at 295–297 mμ (ε 14400). In the p.m.r. spectrum the aromatic protons appeared as three groups, namely, at 7·9–8·2 p.p.m. (1 proton), 7·6–7·9 p.p.m. (2 protons), and 7·0–7·5 p.p.m. (14 protons); and a singlet (1 proton) at 6·87 p.p.m. Reference to the mass spectrum has been made in the Discussion section. Hydrogenation of (VII) at atmospheric pressure in the presence of palladium on carbon in cyclohexane gave 1-(1,2-diphenylethyl)naphthalene (98%), m.p. 82–83°, identified by direct comparison.

Dehydration of 1-(1-Hydroxy-1,2-diphenylethyl)naphthalene and of 1-(trans-*1,2-Diphenylethenyl)-naphthalene*

The carbinol (VI) (1 g), m.p. 150–151° (lit.[10] 149–150°), prepared essentially according to Bauer, was refluxed in anhydrous benzene (50 ml) in the presence of *p*-toluenesulphonic acid (1 g) for 5–6 hr. The crude product formed a pale yellow oil, which was purified by passage through a short bed of alumina (2 by 5 cm) to give a colourless gum (0·85 g). Examination by gas chromatography indicated the presence of two compounds; their ratio varied in different experiments between 1 : 9 and 0·5 : 9·5. An analytical sample of the major component was produced by preparative gas chromatography.

1-(trans-*1,2-Diphenylethenyl)naphthalene* (VIII) (Found: C, 93·7; H, 6·0. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%) formed a colourless gum which could not be induced to crystallize. Its u.v. spectrum exhibited a maximum at 284–286 mμ (ε 13100).

1-(1,2-Diphenylethyl)naphthalene.—A solution in cyclohexane of the mixture (0·1 g) of the olefins (VII) and (VIII) as obtained by dehydration of the carbinol (VI) was hydrogenated (Pd/C; 0·05 g; 5%) to give 1-(1,2-diphenylethyl)naphthalene (V) (0·1 g), which separated from ethanol or methanol in colourless prisms, m.p. 83·5–84° (lit.[11] m.p. 82–83°) (Found: C, 94·0; H, 6·3. Calc. for $C_{24}H_{20}$: C, 93·6; H, 6·5%). Its u.v. spectrum exhibited maxima at 313 (ε 360), 292 (ε 4800), 282 (ε 6800), and 274 mμ (ε 6400); points of inflexion occurred at 264 (ε 4100) and at 254 mμ (ε 2400). (Lit.[11] λ_{max} at 292·5, 283·5, 276, and 273 mμ.) Its p.m.r. spectrum showed a complex multiplet between 7·0 and 8·0 p.p.m. (17 protons) and an ABX system the X part of which was centred at 4·91 p.p.m. ($|J_{AB}+J_{BX}| = 15{\cdot}1$ c/s); the AB part occurred at *c.* 3·41 p.p.m. ($J_{AB} \simeq 13$ c/s). When measured in 1,2,4-trichlorobenzene, the ABX system occurred at 4·98 p.p.m. and 3·37 p.p.m. On heating, this pattern gradually changed into an A_2X pattern, with the X part centred at 5·02 p.p.m. (triplet J 7·3 c/s) and the A_2 part at 3·43 p.p.m. (J 7·3 c/s). This change, which was complete at 160°, was reversed on cooling, when the ABX pattern reappeared.

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[10] Bauer, H., *Ber. dt. chem. Ges.*, 1909, **42**, 2588.

[11] Gilman, H., Brannan, C. G., and Ingham, R. K., *J. org. Chem.*, 1957, **22**, 685.